

Contrails

FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Graphite Materials Development" Project No. 7381 "Materials Application", Task No. 738102 "Materials Pre-production Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, with Captain R. H. Wilson, L. J. Conlon, and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Advanced Materials Laboratory of National Carbon Company, located at Lawrenceburg, Tennessee, under the direction of Mr. R. M. Bushong, Director of the Advanced Materials Project and Mr. R. C. Stroup, Manager of the Advanced Materials Laboratory. This report covers work conducted from May, 1960, through September, 1962.

This is the thirteenth of a series of volumes of WADD Technical Report 61-72 prepared to describe various phases of the work. The preceding volumes of this series are:

- Volume I Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
- Volume II Applications in Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
- Volume III Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystal, by Roger Bacon and Richard Sprague.
- Volume IV Adaptation of Radiographite Principles to the Quality Control of Graphite, by R. W. Wallouch.
- Volume V Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
- Volume VI Creep of Carbons and Graphites in Flexure at High Temperatures, by E. J. Seldin.
- Volume VII High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch.
- Volume VIII Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner
- Volume IX Fabrication and Properties of Carbonized Cloth Composites, by W. C. Beasley and E. L. Piper.

Contrails

- Volume X Thermal Reactivity of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.
- Volume XI Characterization of Binders Used in Fabrication of Graphite Bodies, by E. deRuiter, A. Halleux, V. Sandor, and H. Tschamler.
- Volume XII Development of an Improved Large Diameter Fine-Grain Graphite for Aerospace Applications, by C. W. Waters and E. L. Piper.

ABSTRACT

This report describes the development, fabrication, and physical properties of grade RVC graphite (formerly designated as experimental grade RT-0029). Grade RVC has been manufactured in sizes up to 18 inches in diameter by 15 inches in length and is nominally characterized by a bulk density of 1.81 g/cc, an admittance to N₂ of 2×10^{-2} and 6×10^{-3} cm²/sec. w.g. and a.g. respectively, and a room temperature flexural strength w.g. and a.g. of 2560 and 1930 lbs/in² respectively. RVC is an excellent substrate material for silicon carbide coatings because its thermal expansion between 400 and 1000°C is approximately 0.3 per cent in both grain directions. This expansion is in the same range as that for silicon carbide. Results are also presented on high temperature oxidation of silicon carbide coated grade RVC specimens. The unusually good oxidation protection afforded the graphite by the coating demonstrates the marked superiority of this substrate over other graphite materials which do not match the silicon carbide in thermal expansion.

This report has been reviewed and is approved.



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TABLE OF CONTENTS

	<u>PAGE</u>
1. INTRODUCTION	1
2. COMPOSITION DESIGN	3
2.1. Fluid Coke Trials	4
2.2. Gilsonite Coke Trials	4
2.3. Development of Grade RVC Graphite	8
3. SCALE-UP	12
4. TYPICAL PHYSICAL PROPERTIES OF 18-INCH DIAMETER GRADE RVC GRAPHITE	15
5. OXIDATION AND THERMAL CYCLING TESTS ON COATED MATERIALS	22
6. CONCLUSIONS	24
7. RECOMMENDATIONS	25
8. REFERENCES	26
9. APPENDIX: TEST METHODS FOR THE DETERMINATION OF PHYSICAL PROPERTIES OF GRAPHITE	27

LIST OF FIGURES

FIGURE		PAGE
1.	Fluid Coke Particles, 100X	5
2.	Conventional Coke Particles, 100X	5
3.	Thermal Expansion of Grade ATJ Graphite, With-the-Grain, and of Silicon Carbide	6
4.	Calcined Gilsonite Coke Particles, 100X	7
5.	Close-up of Region Containing Flaw in 18-Inch Diameter Block of Grade RVC Graphite	13
6.	Thermal Expansion of Graphite Grades RVC and ATJ (With-the-Grain) and of Silicon Carbide	15
7.	Thermal Conductivity vs. Temperature, Grade RVC Graphite	17
8.	Porosimetry Curve of Grade RVC Compared to Grade ATJ Graphite.	20
9.	Photomicrographs of Graphite Grades RVC and ATJ, 100X	21
10.	Thermal Cycling Tests on Graphite Grades ATJ and RVC.	23
11.	Photograph Showing Zygo Penetrant Dye and Black Light Test of Silicon Carbide Coated Graphite Grades RVC and ATJ After Thermal Cycling.	25

LIST OF TABLES

TABLE		PAGE
1.	Effect of Polymer Order on Dimensional Changes in Graphitizing	3
2.	Thermal Expansion of Conventional and Fluid Coke-Base Graphites	6
3.	Composition of Filler Component in Experimental Graphite Substrates	9
4.	Physical Properties of Experimental Graphite Substrates.	9
5.	Composition of Grade RT-0028 Graphite.	10
6.	Thermal Expansion of 10-Inch Diameter Grade RT-0028 Graphite	11
7.	Typical Physical Properties of Graphite Grades RVC and ATJ.	16
8.	Flexural Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics	18
9.	Tensile Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics	19
10.	Compressive Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics	19
11.	Representative Thermo-Mechanical Indices	22
12.	Weight Changes During Successive Exposures of Silicon Carbide Coated Graphite Grades RVC and ATJ to Convectively Flowing Air at 1000°C	23

1. INTRODUCTION

The high temperature strength and stability of graphite has made this material extremely important in many aerospace applications. The utilization of the unique high temperature properties of graphite in some applications is handicapped by the susceptibility of graphite to oxidation, beginning at relatively low temperatures. The need for high temperature structural materials in the development of hypersonic aircraft and re-entry vehicles has resulted in considerable attention being given to means of protecting graphite from oxidation at relatively high temperatures.

Bell Aerosystems Company,⁽¹⁾ under Contract AF 33(616)-6043, investigated silicon carbide coated grade ATJ graphite as a candidate material for use to 3000°F in air. Because of the differential thermal expansion between silicon carbide and grade ATJ graphite, failure due to crack formation in the coating occurred during heating and cooling cycles. Although grade ATJ can be used as a substrate for silicon carbide coatings with moderate success, the reliability of the coating is never 100 per cent. Coatings such as TiN, Al₂O₃, B₄C, MoSi₂, Re metal,⁽²⁾ and others have been applied to graphites with little success except when the sample size was small. As a result of these and other investigations, it was concluded that the graphite substrate, not the coating, was the major problem in fabricating coated, oxidation-resistant graphite.

The major deterrent to the successful application of a coating to graphite is the mismatch in thermal expansion between the coating and the substrate. For sufficiently large thermal expansion differences, the coating is cracked by thermal cycling, and the substrate graphite may be materially weakened. To further complicate the problem, most graphites are anisotropic, because of the base materials from which they are derived and the methods by which they are formed. Thus, there exists an inherent mismatch of thermal expansion in different directions within the substrate itself. Until recently, the approach to the problem of applying protective coatings to graphite has been to choose an existing graphite grade whose thermal expansion most nearly matched that of the coating; and to vary the parameters of the coating process to effect a compatible system. No completely successful coating process has been realized through this approach, and all attempts have merely underlined the need for an isotropic graphite substrate whose thermal expansion matches that of the coating to be applied. Therefore, the two prerequisites for a successful graphite substrate are: (1) the graphite must be as nearly isotropic as possible, and (2) its thermal expansion must closely match that of the respective coating.

With the development by National Carbon Company of a successful silicon carbide coating technique⁽³⁾ within the limitations of the then available substrates, development work was initiated in 1959 to produce substrate

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Contrails

graphite grades truly satisfying the above prerequisites. This report describes that work which has led to a graphite, grade RVC, having an isotropic thermal expansion closely matching that of SiC over an extended temperature range. In addition, this grade is characterized by high density and strength combined with low permeability and low elastic modulus.

2. COMPOSITION DESIGN

Most conventional artificial graphites contain petroleum coke-base material as their major ingredient, and for this reason are normally anisotropic. Petroleum coke particles, because of the way in which they are formed, (4) are anisometric and anisotropic. In forming a graphite article, whether by molding or extrusion, these particles (and hence the graphite crystallites of which they are composed) align preferentially, giving rise to the pronounced anisotropy common to most graphite grades.

To further complicate the problem, carbon shapes fabricated from poorly aligned and well aligned cokes exhibit considerable contrast in dimensional change when processed from the baked to the graphitized state, (e.g., 1000 to 3000°C). The terms "poorly aligned" and "well aligned" refer to a relatively high or low with-grain thermal expansion of the final graphite product. With poorly aligned cokes, volume shrinkage is quite high, leading to high graphitized densities and high hardness; with well aligned cokes, volume shrinkages are small and a characteristic length increase occurs upon graphitization. Table 1 shows the volume, diameter, and length changes from 1000 to 3000°C, for rods extruded from poor and well aligned cokes. Table 1 illustrates the very large volume and length shrinkages for the high expansion cokes (from fluoranthene and fluorene) as contrasted to the much lower volume shrinkage and length expansions for the well aligned cokes. Basic considerations in designing a substrate grade, therefore, were choosing raw materials whose structures are isometric and have little or no preferred crystallite orientation, and arriving at a composition whose volume expansion does not preclude fabrication in moderate sizes.

Table 1. Effect of Polymer Order on Dimensional Changes in Graphitizing (5)

Table 1. Effect of Polymer Order on Dimensional Changes in Graphitizing(5)

Starting Material for Coke Filler	Coke Alignment	Graphite Rod Properties			Dimensional Changes, per cent		
		Bulk Density, g/cc	Specific Resistance, 10 ⁴ ohm-cm	Thermal Expansion (20-100°C), per cent	1000 - 3000°C		
					Volume	Diameter	Length
Fluoranthene	poor	1.691	1265	+ 0.045	-15.98	- 5.62	- 5.68
Fluorene	poor	1.522	2640	+ 0.028	-14.46	- 5.98	- 3.23
Acenaphthene	good	1.456	810	- 0.00016	- 3.91	- 2.10	+ 0.26
Acenaphthylene	good	1.396	770	- 0.0016	- 3.22	- 1.84	+ 0.44
Low Sulfur Thermal Tar	good	1.485	730	+ 0.00028	- 4.30	- 2.31	+ 0.28

2.1. Fluid Coke Trials

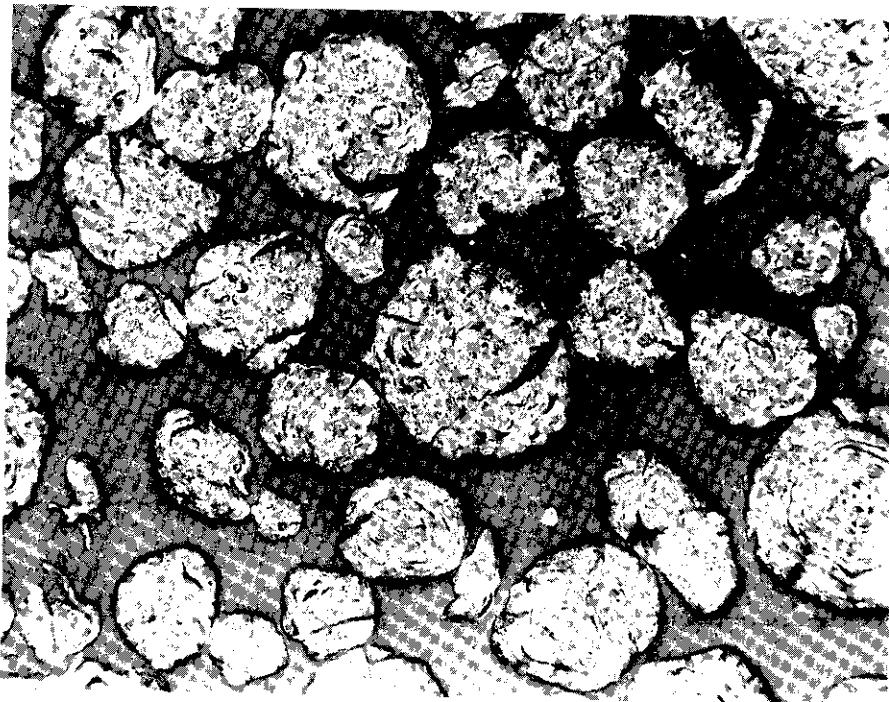
Fluid coke is a material whose basic structure is isometric, being made of spherical concentric shells of pyrolytically deposited carbon. A photomicrograph of this material is presented in Figure 1. A photomicrograph of conventional coke particles has been presented in Figure 2 for comparison. Initial attempts at fabrication utilized fluid coke, artificial graphite flour, and minor quantities of gas black as filler material. The binder was coal tar pitch.

Forming was accomplished by the pressure curing technique using a thermosetting binder instead of the usual thermoplastic binder. This type of processing, which was developed for grade RVA graphite, is described in an earlier report of this series. ⁽⁶⁾ In brief, sulfur is added to the blend to react with the pitch as the charge is heated by electrical resistance in an insulated mold under approximately 1000 lb/in² molding pressure. The reaction results in a thermoset body at relatively low temperature (of the order of 300°C), and facilitates baking without distortion and with reduced volatile evolution. Pieces of this material were cured in a 4-inch diameter mold, baked to 750-800°C, and graphitized at 2800°C. The thermal expansion as a function of temperature was measured up to 1000°C on specimens cut with and across the grain. Table 2 lists the thermal expansion of fluid coke-base graphite compared with conventional molded and extruded stock. The expansion of the fluid coke-base graphite is nearly isotropic compared to conventional graphites, but considerably under the 0.3 per cent expansion of SiC obtained from Figure 3. The fluid coke-base graphite was very difficult to process and nearly all of the blocks cracked because of high shrinkage and poor thermal properties of the filler.

Although thermal expansion is nearly parabolic with temperature and curves concavely upward to 400°C, from this temperature to 1000°C the change in specimen length is nearly linear with temperature. This behavior is shown in Figure 3 by a thermal expansion curve for grade ATJ graphite. The total thermal expansion in the 400-1000°C range was measured and used as an index of the compatibility of prospective substrate materials for SiC coating. The thermal expansion of silicon carbide in this temperature range is 0.30 to 0.31 per cent, as shown in Figure 3.

2.2. Gilsonite Coke Trials

Coincident with this work with fluid coke, forming trials utilizing calcined gilsonite coke as the filler material were also in progress. Gilsonite is a naturally occurring asphaltic material which, after carbonization, exhibits a poorly crystalline cross-linked structure. Figure 4 is a photomicrograph of calcined gilsonite coke particles showing the fluffy, sootlike character of this material. Pieces were both molded and extruded from various mix compositions containing graded gilsonite coke particle sizings with coal tar pitch binder. After baking and graphitization, the thermal expansions were measured over the 400-1000°C range and found to be 0.38 per cent with the grain and 0.43 per cent across the grain. The expansions therefore were



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Figure 1. Fluid Coke Particles, 100X

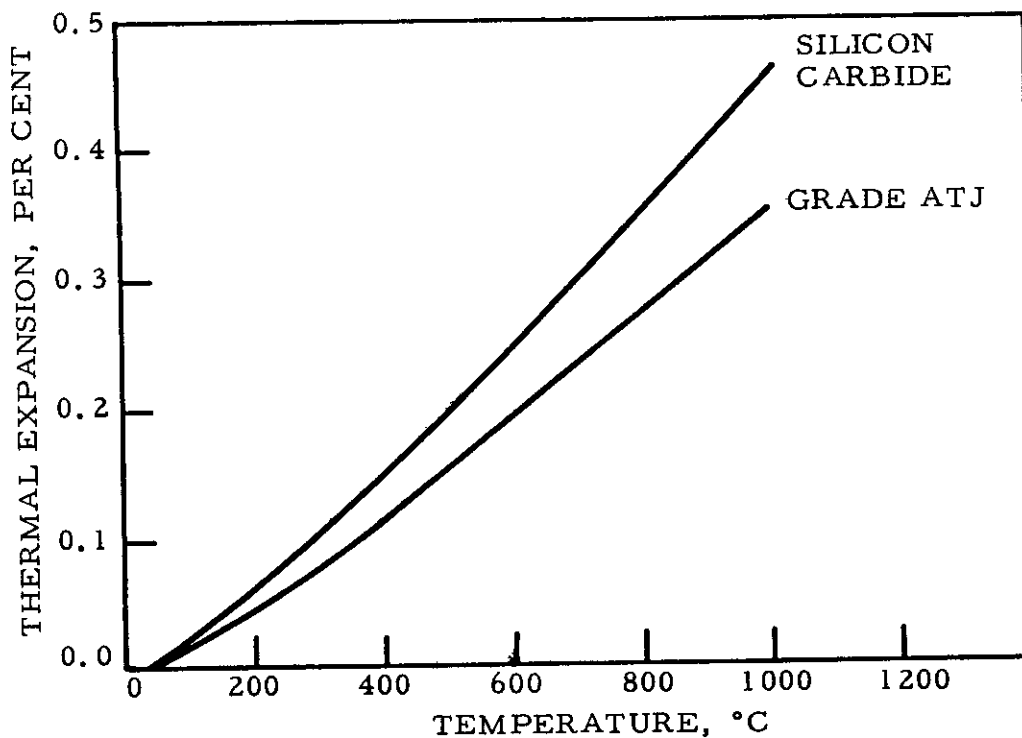


Figure 2. Conventional Coke Particles, 100X

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Table 2. Thermal Expansion of Conventional
and Fluid Coke-Base Graphites

Graphite Grade	Orientation	Thermal Expansion Per Cent (400 - 1000°C)
Fluid Coke-Base (Molded)	With-the-Grain	0.25
	Across-the-Grain	0.28
ATJ (Molded)	With-the-Grain	0.24
	Across-the-Grain	0.31
CS 312 (Extruded)	With-the-Grain	0.23
	Across-the-Grain	0.33



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Figure 3. Thermal Expansion of Grade ATJ Graphite,
With-the-Grain, and of Silicon Carbide



N-3696

Figure 4. Calcined Gilsonite Coke Particles, 100X

higher than that for silicon carbide. Blocks made using only calcined gilsonite as the filler material could not be processed in sizes sufficient for normal use because of the large (8 to 10 per cent) volumetric shrinkage in processing.

2.3. Development of Grade RVC Graphite

From a comparison of the thermal expansions of graphites made from graphitized fluid coke and that made from calcined gilsonite, it became apparent that a combination of these two raw materials should produce the desired thermal expansion. The subsequent work was then focused upon finding the proper mix formulation to give a thermal expansion equal to or slightly above that of the coating and which could be processed without flaws.

Seven experimental grades were processed from combinations of gilsonite, fluid coke, metallurgical coke, petroleum coke-base graphite and carbon black. The ingredients were used in a series of materials with varying thermal expansions. These compositions are shown in Table 3. Three forming methods were employed: pressure baking (NT), ⁽⁷⁾ in which the blend is placed under pressure in a mold and heated by electrical resistance to 800°C; pressure curing (RT); ⁽⁶⁾ and extrusion (L). After graphitization, physical properties were determined on each of these grades and the results are tabulated in Table 4. It will be noted that the RT materials have a thermal expansion somewhat lower than the desired 0.3 per cent in the 400-1000°C range, while the L series is somewhat higher. Silicon carbide coated samples of all seven grades were tested for oxidation resistance at 600°C at the Oak Ridge National Laboratory. The importance of the thermal expansion match between coating and substrate is borne out by the fact that "only sample NT-0056 was completely oxidation resistant after 76 hours of testing in air at 600°C". ⁽⁸⁾ In our own tests, samples of RT-0026 and L-928 were machined into tubes, silicon carbide coated, and heated in air at 1000°C. Vertical cracks in the coating developed on the RT-0026 substrate, typical of those seen when the thermal expansion of the substrate was appreciably less than that of the coating. This is a result of the fact that the coating was under tension exceeding its ultimate strength upon cooling after the coating process. In the case of L-928, the only flaws that developed were at the ends of the cylinder at the corners. This type of flaw is attributed to concentration of stress at sharp changes in geometry due to an excessive mismatch of the thermal expansion.

It was apparent at this stage that the desired thermal expansion of 0.3 per cent was bracketed by the pressure cured (RT) compositions on the low side and the extruded (L) compositions on the high side and that a decision had to be made as to which method of processing to pursue. Although grade NT-0056 was satisfactory from the standpoint of oxidation resistance, it will be noted from Table 3 that its flexural strengths are comparatively low.

In conventional extrusion, the carbon filler materials are mixed with coal tar pitch at an elevated temperature, extruded as a thermoplastic mass, and thermally treated to convert the binding material to carbon. During the thermal processing cycle, the very nature of the thermoplastic material introduces problems. The mass, which possesses good plasticity for forming,

Table 3. Composition of Filler Component in Experimental Graphite Substrates

Grade	Maximum Particle Size Inch	Per Cent of Filler				
		Fluid Coke	Pet. Coke Graphite	Metallurgical Coke	Gilsonite Coke	Carbon Black
RT-0025	0.03	50	43	--	--	7
RT-0026	0.03	40	52	--	--	8
RT-0027	0.03	40	--	45	--	15
NT-0056	0.03	50	--	--	50	--
L-926	0.06	--	--	--	100	--
L-927	0.03	--	--	--	100	--
L-928	0.015	--	--	--	100	--

Table 4. Physical Properties of Experimental Graphite Substrates

Grade	Bulk Density g/cc	Specific Resistance 10 ⁻⁴ ohm-cm		Young's Modulus 10 ⁶ lb/in ²		Flexural Strength lb/in ²		Thermal Expansion, Per Cent			
		w. g.	a. g.	w. g.	a. g.	w. g.	a. g.	25 - 100°C		400 - 1000°C	
RT-0025	1.75	21.0	21.0	1.1	1.0	2260	2360	--	--	0.27	0.264
RT-0026	1.74	34.0	30.0	1.3	1.2	2840	2530	--	--	0.246	0.276
RT-0027	1.71	31.0	25.0	1.1	0.8	2170	1740	0.02	0.03	0.0258	0.27
NT-0056	1.56	12.0	16.0	0.5	1.2	1140	520	0.024	0.0277	0.288	0.318
L-926	1.58	15.3	15.0	1.1	1.1	2860	3110	0.0345	0.0375	0.372	0.396
L-927	1.62	13.6	14.1	1.2	1.2	3100	3270	0.0352	0.039	0.378	0.408
L-928	1.65	12.6	15.0	1.4	1.4	3710	2420	0.0337	0.039	0.366	0.408

becomes even softer when heated further to carbonize, and would completely lose its shape if it were not supported during the bake. Also, at about the time when it is most plastic, large quantities of gas are evolved - about 20 times the original volume. After this point, further heating causes binder carbon to shrink or decrease in volume. This shrinkage also must be controlled and held uniform throughout the article, otherwise, cracking or distortion results. With the abnormally high shrinkage obtained with gilsonite coke and fluid coke it is questionable whether sizes larger than 6 inches in diameter could be produced by conventional methods. The pressure curing process avoids one of the basic difficulties in the conventional methods; i. e., the swelling and disruption of the product by pressure of the volatiles. Shrinkage remains a problem in both pressure curing and extrusion, but the uniformity of heating in the pressure curing process tends to avoid nonuniform shrinkage and product disruption. On this basis, extrusion was ruled out as a forming method for substrate material and all subsequent trials utilized the pressure curing process.

The work utilizing the pressure curing technique was done in 10-inch diameter sizes to find a blend that would produce isotropic graphite with the desired thermal expansion and to investigate processing difficulties which could arise in scaling up the size of graphites made from these unconventional filler materials. The mix design and forming conditions were varied until an optimum composition was achieved. This combination, after curing, baking, and graphitization, resulted in experimental grade RT-0028. The final composition is given in Table 5.

Table 5. Composition of Grade RT-0028 Graphite

	Per Cent by Weight
Fluid Coke Particles (through 35 mesh)	12.1
Gilsocarbon Particles (through 10 on 30 mesh)	20.3
Gilsocarbon Flour	31.4
Petroleum Coke-Base Graphite Flour	10.4
Carbon Black (Thermax)	6.7
175°C M. P. Coal Tar Pitch	15.8
Sulfur	3.3

Table 6 lists the thermal expansion of grade RT-0028 and shows both the isotropy and the expansion levels to be very nearly those which are desirable in a substrate graphite for SiC coating.

Table 6. Thermal Expansion of 10-Inch Diameter Grade RT-0028 Graphite

Orientation	Thermal Expansion, Per Cent (400°-1000°C)
With-the-Grain	0.324
Across-the-Grain	0.342

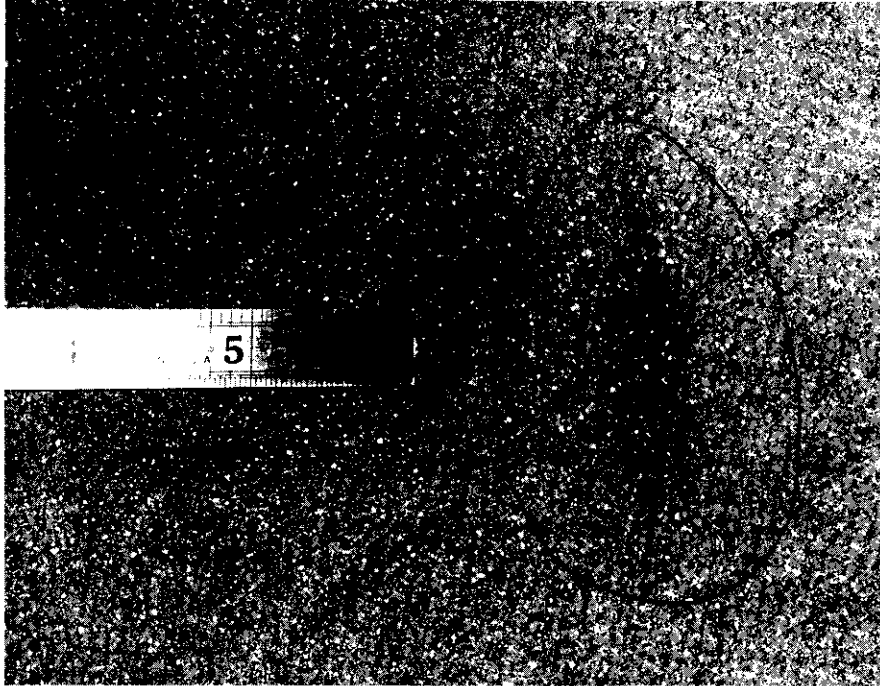
Vought Astronautics Division of Ling-Temco-Vought tested the oxidation resistance of SiC coated grade RT-0028 graphite samples cut from the 10-inch diameter material with excellent results.

3. SCALE-UP

Having determined the proper mix formulation, the next steps in the development of grade RT-0028 graphite were to investigate the problems of "scale-up" and to fabricate sizes large enough for useful hardware. The size chosen for this development phase was 18-inch diameter since it was sufficiently large to produce full-scale hardware as well as to give an insight into the problems of producing even larger sizes. Composition and processing details for the 18-inch diameter trials followed the earlier experience as closely as possible with the exception that after the baking operation, the block was pitch impregnated and rebaked before graphitization. These additional steps were performed to increase the strength of this grade. The experimental grade number was changed to RT-0029 which has now been designated grade RVC. Several blocks, 18-inch diameter by approximately 16-inch length, were pressure cured with no apparent processing difficulties. The ingredients were blended at room temperature, charged into an electrically insulated mold lined with a porous electrically conductive envelope completely surrounding the blend, and heated under pressure to temperatures of the order of 300°C. No visual flaws were apparent when this stock was sectioned in the cured state.

During this development program, the work was coordinated closely with a contractor for a nose cap application. The contractor tested the oxidation resistance of SiC coated grade RT-0029 samples cut from the 10-inch diameter material with excellent results, and therefore requested 24-inch diameter stock for full scale testing. The contractor indicated that the request was urgent because of a close program schedule. The problems involved in pressure curing RT-0029 appeared under control, and while several of the 18-inch diameter billets were being processed through baking, impregnation, and graphitization (requiring approximately 12 weeks), scale up to 24-inch diameters was undertaken. Several pieces of 24-inch diameter grade RT-0029 were formed by the same technique employed in fabricating the 18-inch diameter stock, again with no apparent flaws in the cured state.

While the 24-inch trials were in process, some of the 18-inch blocks were cut open and examined after having completed the baking operation. The structure of this material appeared to be excellent everywhere except in a highly localized region near the center, where some of the blocks were cracked or structurally weak. Figure 5 is a close-up of the region containing a typical flaw found in one of the baked pieces. Subsequently, in the finished 18-inch graphitized stock, these imperfections became more severe. Since development problems are materially increased as the diameter of product increases, it was not wholly unexpected that of the 16 billets of 24-inch diameter stock formed, only one survived the baking operation. The decision was made to continue this program in the 18-inch diameter size, particularly since it was ascertained that the 18-inch size would be adequate for full scale testing.



N-3697

Figure 5. Close-up of Region Containing Flaw in 18-Inch Diameter Block of Grade RVC Graphite

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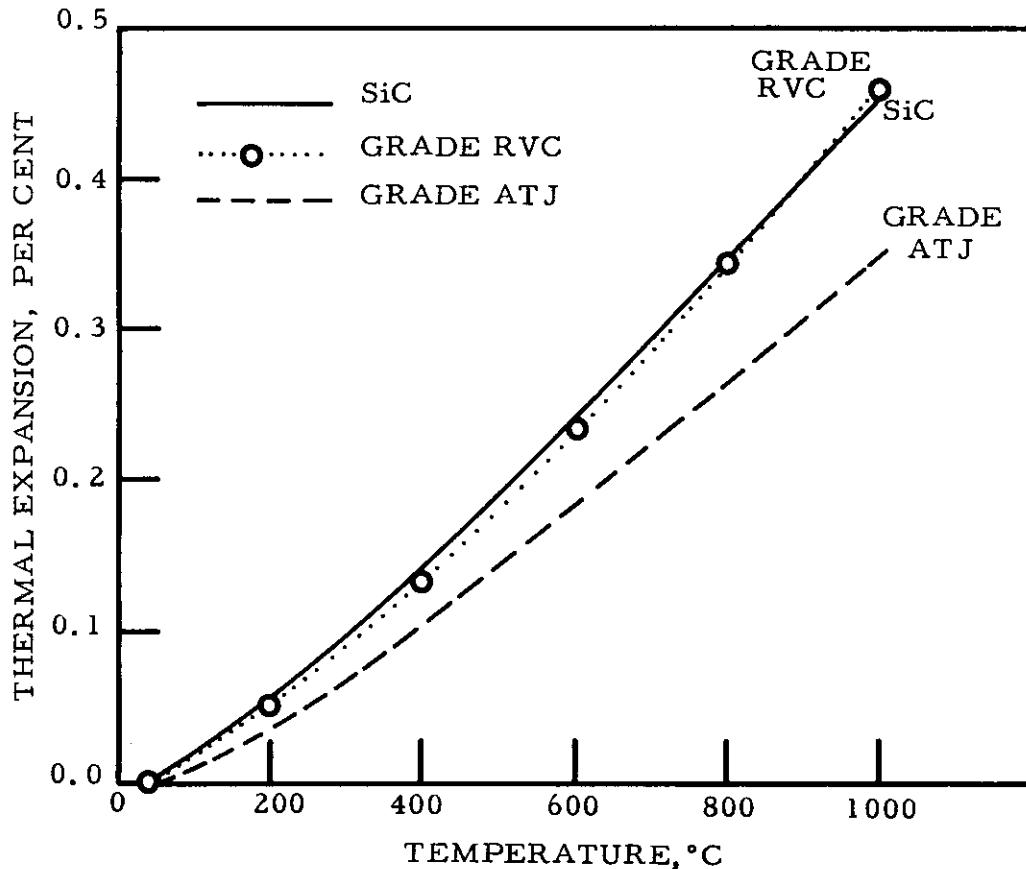
A weak center or flaw, running perpendicular to the axis of the cylinder, was the basic problem encountered in the fabrication of the large diameter grade RVC graphite. These cracks probably originated as weak areas in the curing or baking operation, but in some cases they were not visible until after graphitization. From previous development work with grade RVA graphite, ⁽⁶⁾ it was recognized that this type of flaw arose from nonuniformity of curing temperatures. When the curing temperature is considerably higher at the periphery of the stock than at its axis, such an internal flaw is usually generated. Therefore, the first approach in solving the cracking problem was an attempt to minimize any differential in curing temperature by increasing the resistance of the porous envelope from that used in the 10-inch diameter blocks. Thermocouples placed at the center and periphery of one of these pieces during the cure showed that the temperature differential was less than 20°C throughout the curing cycle. This degree of uniformity of curing temperature, achieved by increasing the resistance of the porous envelope and accompanied by the use of slower heating rates throughout baking and graphitization, reduced the frequency of flaws so that over 50 per cent of the stock was flaw-free.

Three modified methods of forming grade RT-0029 were attempted unsuccessfully. One piece of 24-inch material made with a furane plasticized pitch binder ⁽⁹⁾ was cut open after graphitization and contained many small, randomly oriented flaws. An attempt to pressure mold five pieces of RT-0029 blend using 110°C pitch and no sulfur failed because of the difficulty in attaining uniform mix temperature when heating electrically in the mold. Overheating in the center caused vertical cracking. Two pieces were made using a mixing device with an oil heated cylindrical shell containing an axially positioned rotating shaft on which were mounted 52 blades pitched to advance the blended charge through the heated cylinder. In this way the heating operation was accomplished without balling. However, the difficulty with these pieces, as with some of the others, was removal from the rough ceramic mold, and they were cracked horizontally in the stripping operation.

4. TYPICAL PHYSICAL PROPERTIES OF 18-INCH DIAMETER GRADE RVC GRAPHITE

The with-grain thermal expansion curves for grades RVA, ATJ and for silicon carbide are shown in Figure 6 which illustrates the extremely close match in thermal expansion between the coating and the substrate.

Although a thermal expansion compatible with the coating is the prime requirement for a substrate graphite, other physical properties are also important in order for it to be considered as an engineering material. Of most concern are the mechanical properties, particularly if the coated graphite is to be used as a structural member. The degree of uniformity must also be such that design can be accomplished with minimum limits of uncertainty. Table 7 lists the average values and standard deviations for the physical properties of grade RVC along with those of standard grade ATJ graphite for comparison.



N-4576

Figure 6. Thermal Expansion of Graphite Grades RVC and ATJ (With-the-Grain) and of Silicon Carbide

Table 7. Typical Physical Properties of Graphite Grades RVC and ATJ

Property, Units	Orientation	N	Grade RVC		Grade ATJ*	
			Av.	Std. Dev.	Av.	Std. Dev.
Bulk Density, g/cc	----	35	1.81	0.010	1.73	0.036
Specific Resistance, 10^{-4} ohm-cm	w.g.**	20	12.60	0.28	11.00	1.68
Young's Modulus, 10^6 lb/in ²	a.g.	11	14.20	0.26	14.50	1.45
	w.g.	20	0.73	0.02	1.45	0.166
Flexural Strength, lb/in ²	a.g.	11	0.62	0.03	1.15	0.95
	w.g.	20	2560	190	4010	773
Compressive Strength, lb/in ²	a.g.	49	1930	262	3580	484
	w.g.	13	13,425	1075	8270	1028
Tensile Strength, lb/in ²	a.g.	14	13,450	825	8540	1144
	w.g.	10	2520	183	3160	----
Mean Coefficient of Thermal Expansion, $10^{-6}/^{\circ}\text{C}$ (400-1000 $^{\circ}\text{C}$)	a.g.	10	1677	354	2950	----
	w.g.	4	5.2	----	4.0	----
Mean Coefficient of Thermal Expansion, $10^{-6}/^{\circ}\text{C}$ (30-100 $^{\circ}\text{C}$)	a.g.	4	5.1	----	5.2	----
	w.g.	4	3.4	----	2.2	0.216
Thermal Conductivity, cal-cm/sec-cm ² $^{\circ}\text{C}$ (room temperature)	a.g.	4	3.8	----	3.4	0.223
	w.g.	2	0.203	----	0.281	----
Admittance to N ₂ , cm ² /sec.	a.g.	2	0.183	----	0.214	----
	w.g.	2	2×10^{-2}	----	3×10^{-1}	----
Ash, wt. per cent	a.g.	2	6×10^{-3}	----	3×10^{-1}	----
	----	1	0.159	----	0.158	0.038

* Data from The Industrial Graphite Engineering Handbook, National Carbon Company, Rev. 5/62, except for tensile strength which was determined as described in paragraph 6 of the Appendix to this report.

** w.g. - with-the-grain a.g. - across-the-grain

Thermal conductivity at elevated temperatures has been determined by both Southern Research Institute⁽¹⁰⁾ and the National Carbon Research Laboratory. These results are shown in Figure 7. Reasonable agreement was obtained between the two laboratories with the thermal conductivity leveling off at 0.07 to 0.10 cal-cm/sec cm² °K above 1000°C. These values compare favorably with those of grade ATJ in the same temperature range.

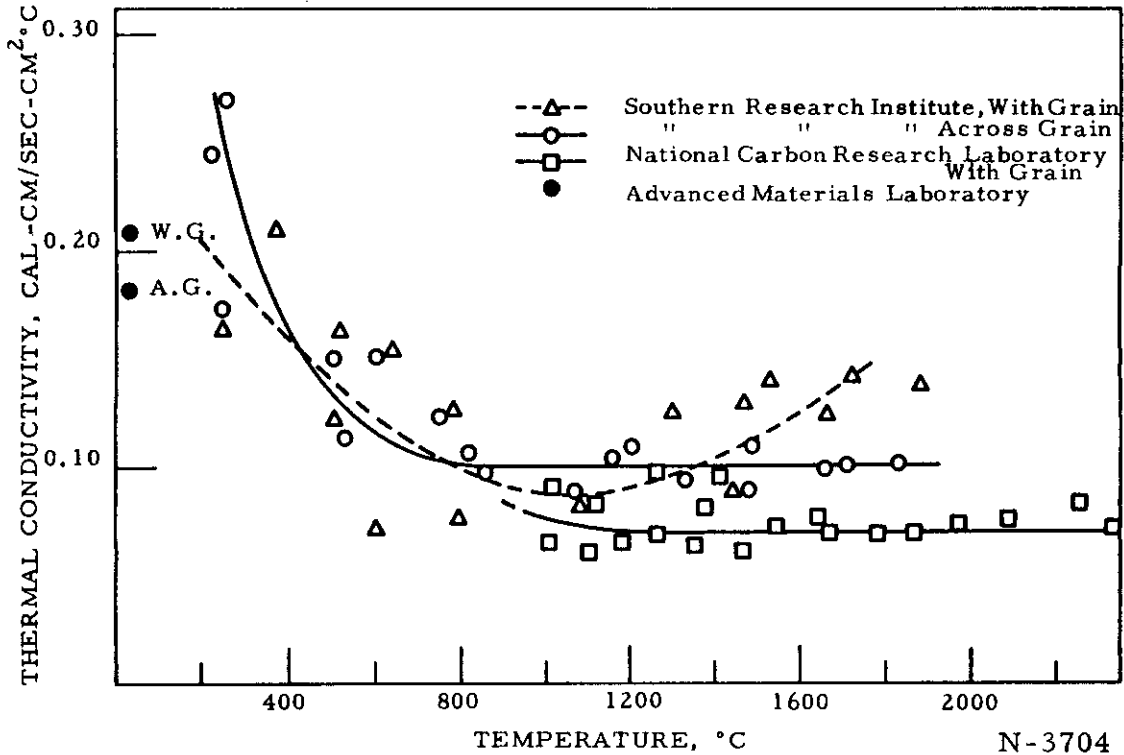


Figure 7. Thermal Conductivity vs. Temperature, Grade RVC Graphite

Limited room and high temperature strength measurements have been made on both uncoated and silicon carbide coated specimens of grade RVC graphite at Vought Astronautics Laboratories.⁽¹¹⁾ The results of these tests are given in Tables 8, 9, and 10. These room temperature tests on uncoated specimens confirm the values determined at the Advanced Materials Laboratory (Table 7) with regard to flexural strength and tensile strength. Vought Astronautics reported a higher modulus of elasticity which can be explained by geometry and positioning of the sample during measurement. The samples are 1 inch x 1-1/2 inch x 8 inches and if the measurement is taken on the 1-1/2 inch by 8 inch surface, the value is higher than if it is measured on the 1 inch by 8 inch surface. It cannot be explained why Vought Astronautics found the compressive strength to be less than that measured at the Advanced Materials Laboratory.

Figure 8 compares the pore size distribution and volume in grade RVC material with conventional grade ATJ stock. As can be seen, the RVC graphite has substantially fewer pores especially in the larger sizes.

A photomicrograph of grade RVC graphite is compared in Figure 9 with one of grade ATJ at the same magnification. It shows the spherical particles of gilsonite coke (the large sphere) and fluid coke (the small spheres) in their normal relationship and sizing.

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Table 8. Flexural Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics

Material	Dimensions Inch	Grain Ori- en- ta- tion	Temper- a- ture	No. of Samples	Flexural Strength	
					Max/Min lb/in ²	Av. lb/in ²
Uncoated	1x1-1/2x8	With Across	RT	3	2990/2730	2867
			RT	3	2080/1880	1976
SiC Coated	1x1-1/2x8	With Across	RT	8	3500/2470	2860
			RT	9	3320/2320	2842
SiC Coated with Holes Drilled	----	With Across	RT	3	3220/2700	2933
			RT	2	3230/2830	----
SiC Coated	1/2x1-1/2x8	With Across	RT	5	3550/3080	3344
			RT	5	4190/3320	3756
SiC Coated	1-1/2 x 1-1/2x8	With Across	RT	5	3150/2280	2728
			RT	5	2980/2300	2552
SiC Coated, Oxidation Tested Be- fore Flexure Test	----	With Across	RT	4	2960/2290	2505
			RT	4	2490/2080	2247
SiC Coated	----	With Across	1000° F	2	3050/2640	2845
			1000° F	3	2970/2800	2890
SiC Coated	----	With Across	2000° F	3	3190/2960	3040
			2000° F	3	2880/2670	2810
SiC Coated	----	With Across	3000° F	3	4250/2780	3603
			3000° F	3	4270/3250	3920

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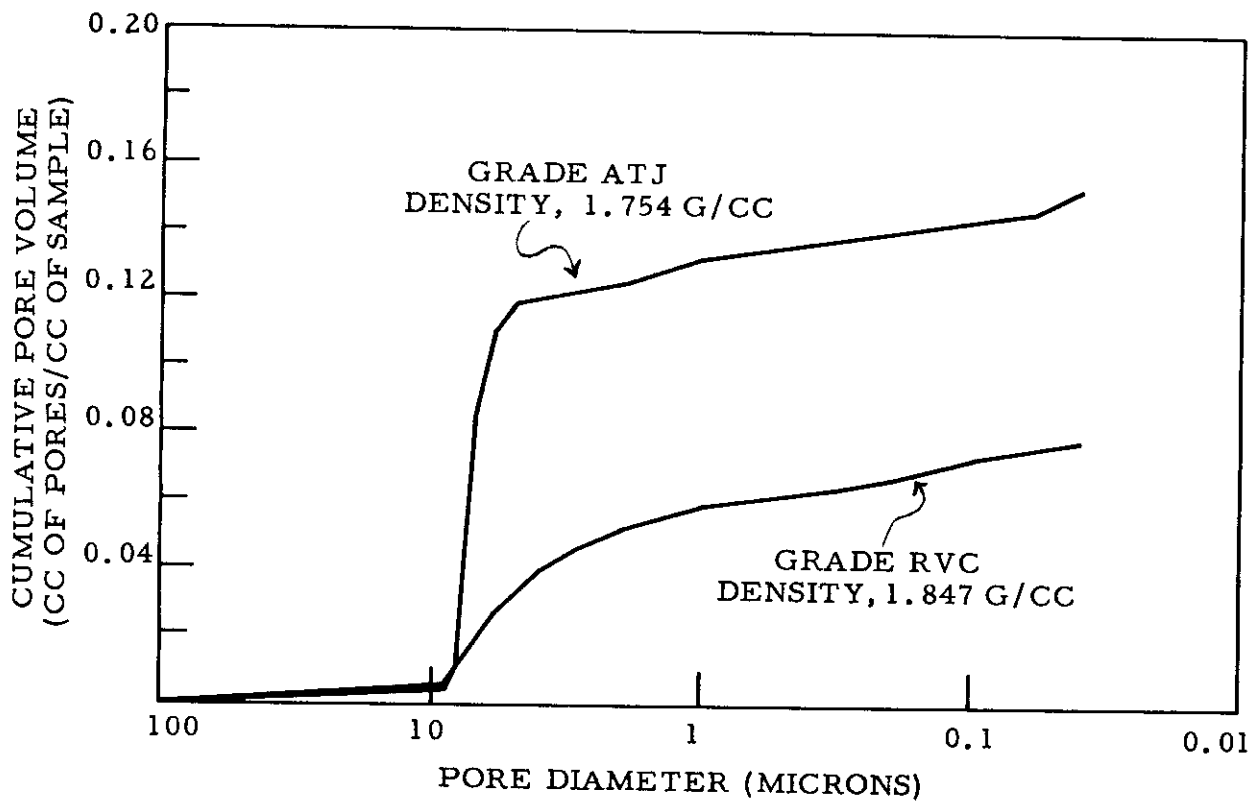
Table 9. Tensile Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics

Material	Grain Orientation	Number of Samples	Temperature	Tensile Strength		Modulus of Elasticity lb/in ²
				Max / Min lb/in ²	Av.	
Uncoated RVC	Across	6	RT	2080/1180	1660	1.30 x 10 ⁶
SiC Coated RVC	With	13	RT	1900/1130	1595	-----
	Across	12	RT	2160/1260	1770	-----

Table 10. Compressive Strength of Uncoated and Silicon Carbide Coated Grade RVC Graphite Determined by Vought Astronautics

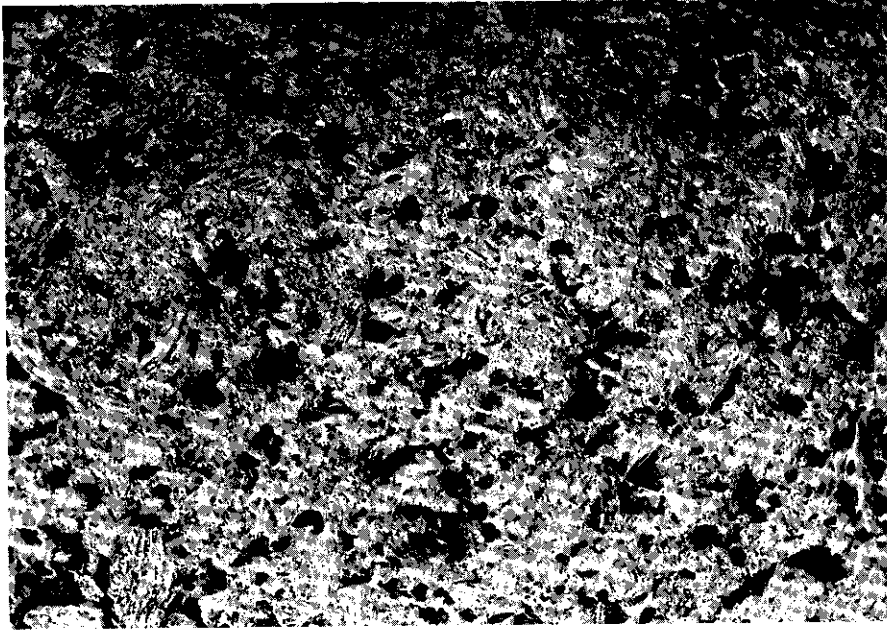
Material	Grain Orientation	No. of Samples	Temperature	Compressive Strength		Modulus of Elasticity lb/in ²
				Max / Min lb/in ²	Av.	
Uncoated RVC	With Across	4	RT	10000/8110	9263	0.749 x 10 ⁶
		3	RT	10400/10200	10267	1.07
SiC Coated RVC	With Across	8	RT	8780/7840	8050	1.200
		5	RT	8580/6010	7170	0.909
SiC Coated RVC	With Across	3	1000°F	7920/7830	7863	0.900
		3	1000°F	7110/6740	6877	0.835
SiC Coated RVC	With Across	2	2000°F	9240/8520	-----	0.925
		2	2000°F	8850/7270	-----	1.270
SiC Coated RVC	With Across	2	2500°F	6740/5790	-----	0.950*
		2	2500°F	7000/5050	-----	0.890

* Only one determination.



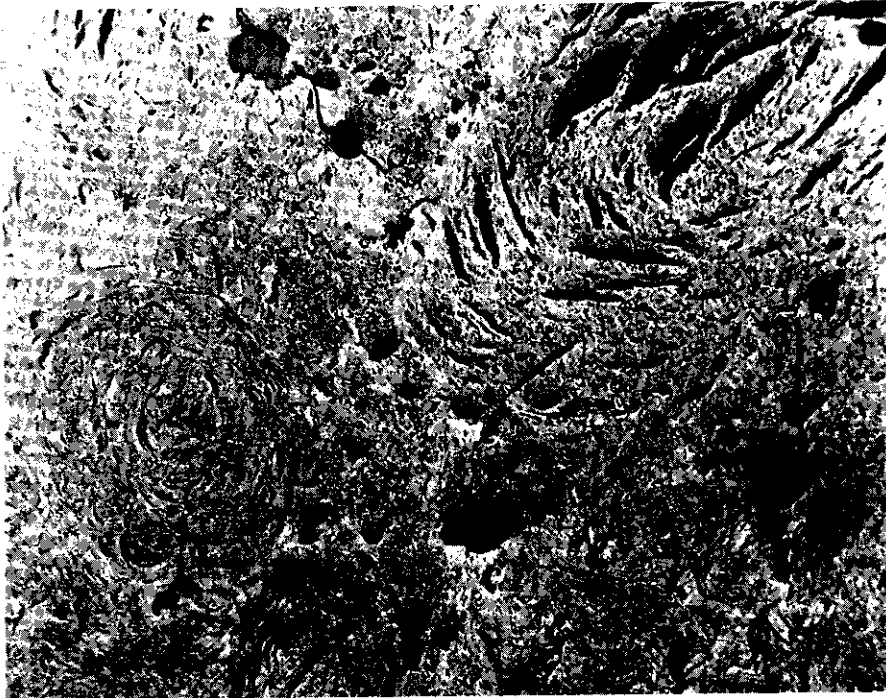
N-3705

Figure 8. Porosimetry Curve of Grade RVC Compared to Grade ATJ Graphite



N-3698

Grade ATJ



Grade RVC

Figure 9. Photomicrographs of Graphite Grades RVC and ATJ, 100X

No meaningful measurements of thermal shock or stress resistance are available on grade RVC graphite at this time. However, since many of its potential applications are strongly dependent on satisfactory behavior under transient or steady-state thermal gradients, some indication of these properties is advantageous. Although they are obviously an over-simplification, and do not fully account for orientation and geometry effects, temperature dependence, or anelasticity, the parameters $KS/\alpha EC_P$ and $S/\alpha E$ are often used as crude indices of thermal shock and stress resistance. In these expressions, K is the thermal conductivity, S the ultimate tensile strength, α the thermal expansion coefficient, E the Young's modulus, and C_P the specific heat at constant pressure. As an indication of relative values, Table 11 gives these two parameters calculated for several graphites and refractories. Room temperature values have been used throughout, and in the case of anisotropic materials, with-grain values for all properties except the thermal conductivity.

Table 11. Representative Thermo-Mechanical Indices

Material	Thermal Shock Index: $\frac{KS}{\alpha EC_P}$ (cm ² °C/sec)	Thermal Stress Index: $\frac{S}{\alpha E}$ (°C)
Graphite: RVC	940	1020
RVA	1060	1000
ATJ	1200	1120
AGR	1860	1350
Refractories: SiC	19	110
BeO	61	36
Al ₂ O ₃	7.3	122

It will be noted that the indices for the three missile grades (RVC, RVA, and ATJ) fall below a highly shock-resistant electrode graphite (AGR), but are in an entirely different and superior class than typical refractory compounds.

5. OXIDATION AND THERMAL CYCLING TESTS ON COATED MATERIALS

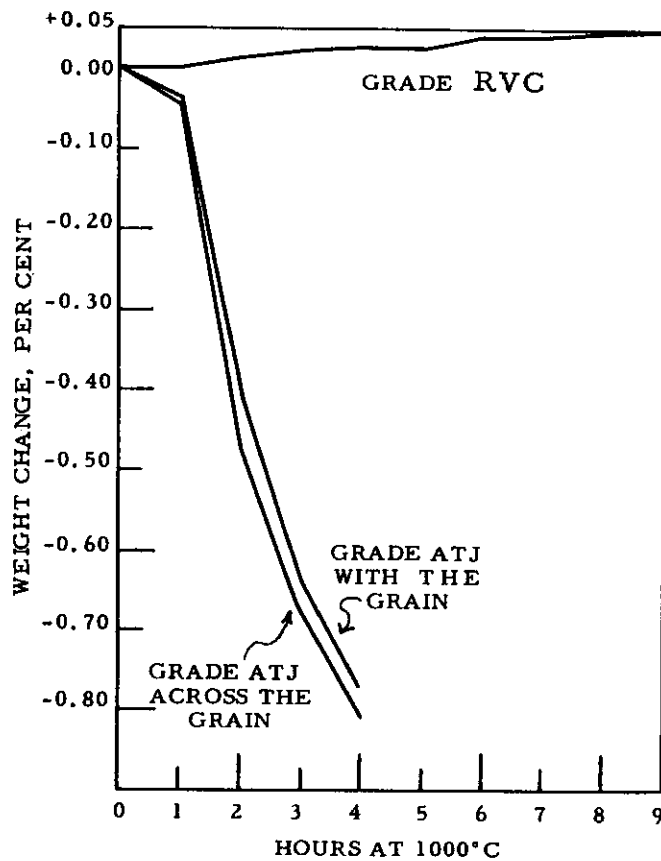
Silicon carbide coated bars of grades RVC and ATJ graphite (1 x 1-1/2 x 8-inch) were subjected to oxidation tests. In these tests, the samples were repeatedly placed in a preheated furnace for one hour at 1000°C, then removed and allowed to cool to room temperature. The samples were weighed to determine weight loss or gain through oxidation. This was repeated up to 18 times on the RVC sample. The results of a typical test are given in Table 12.

A plot of weight change vs. time is presented in Figure 10. As can be seen, the silicon carbide coated grade ATJ sample lost appreciable weight throughout testing, indicating failure of the coating. The coated grade RVC

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Table 12. Weight Changes During Successive Exposures of Silicon Carbide Coated Graphite Grades RVC and ATJ to Convectively Flowing Air at 1000°C

Hours at 1000°C	Coated Grade RVC		Coated Grade ATJ	
	Weight g	Weight Change Per Unit Area mg/cm ²	Weight g	Weight Change Per Unit Area mg/cm ²
0	368.70	0	338.95	0
1	368.70	0	338.80	-0.55
2	368.75	+0.18	337.39	-5.6
3	368.79	+0.32	336.63	-8.4
4	368.80	+0.36	336.20	-9.9
5	368.80	+0.36		
6	368.85	+0.54		
7	368.85	+0.54		
8	368.87	+0.61		
9	368.87	+0.61		
18	368.87	+0.61		



N-3706

Figure 10. Thermal Cycling Tests on Graphite Grades ATJ and RVC

gained weight due to oxidation of the coating to SiO_2 . No coating failure could be detected after eighteen hours of testing.

Two experimental bars of silicon carbide coated grade RVC graphite ($1 \times 1\frac{1}{2} \times 8$ -inch), one with-the-grain (w.g.) and one across-the-grain of molding (a.g.), were supplied to Vought Astronautics for thermal testing. Results were reported as follows: (11)

Orientation	Exposure Conditions	Observations
a.g.	1500° F for 15 min.	Visual check for cracks/none evident.
w.g.	1500° F for 15 min.	Visual check for cracks/none evident.
a.g.	2000° F for 1 hour in air	Slight weight gain.
w.g.	2000° F for 1 hour in air	Slight weight gain.
a.g.	2500° F for 1 hour in air	The flexural strength was 2000 lbs/in ² at room temperature.
w.g.	2500° F for 1 hour in air	The flexural strength was 2200 lbs/in ² at room temperature.

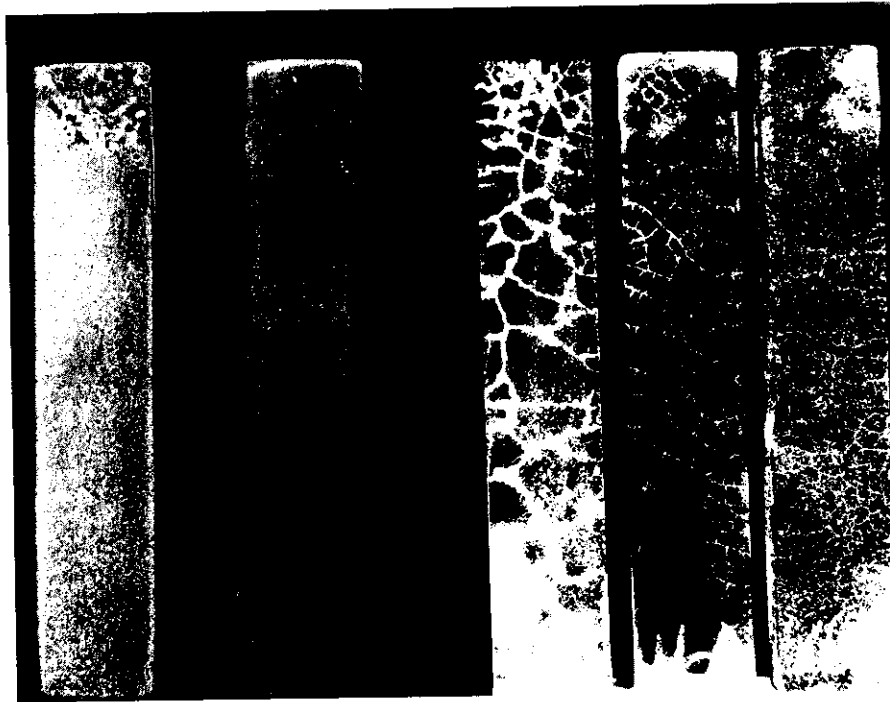
The flexural strengths of the exposed samples are within the normal range of grade RVC graphite and hence indicate no oxidation of graphite occurred under the coating. Figure 11 is a photograph taken after oxidation testing of silicon carbide coated grades RVC and ATJ. The use of Zyglo penetrant dye and black light reveals the absence or presence of crazing in the coat effected by the match or mismatch in thermal expansion between coating and substrate. The difference between the RVC and ATJ is obvious.

Although grade RVC has not been evaluated with materials other than silicon carbide, it is possible that it may be a good substrate for coatings of ZrSiO_4 , HfB_2 and TiB_2 which have thermal expansions near that of the RVC graphite.

6. CONCLUSIONS

On the basis of the work described above, the following conclusions can be made:

- 1) It is possible to produce in useful sizes a fine-grain graphite having a high degree of isotropy, and having a thermal expansion closely matching that of silicon carbide.
- 2) When used as a substrate material for a silicon carbide coating, the resultant composite has exhibited negligible oxidation during extended tests at 1000°C, and shows no tendency to crack, craze, or spall under thermal cycling.
- 3) More general tests of several materials or substrates imply that the optimum performance is attained when the coating is under moderate compression, i. e., the thermal expansion of the substrate should be equal to or slightly higher than that of the coating.



Grade RVC

Grade ATJ

N-3699

Figure 11. Photograph Showing Zyglo Penetrant Dye and Black Light Test of Silicon Carbide Coated Graphite Grades RVC and ATJ after Thermal Cycling

7. RECOMMENDATIONS

1. Future evaluation of the present grade, RVC, is required to fully demonstrate its applicability to aerospace applications. This will include tests under actual or simulated environmental condition, laboratory tests on thermal shock and stress resistance, and compatibility with refractory coatings other than silicon carbide.
2. Process variations, such as curing pressure and pressing techniques, are being evaluated in an effort to increase the yields in the production of this grade of graphite.
3. Variations in the present blend formulation are being investigated in an effort to produce a graphite having the same desirable properties as grade RVC with higher yields. In addition, a scale-up in size should be possible with a blend variation.
4. A complete characterization of properties will be made on grade RVC using material from a laboratory semiproduction run.

8. REFERENCES

1. Anthony, F. M. and Mistretta, A. L., WADD Technical Report 57-744, Volume VIII, "Investigation of Feasibility of Utilizing Available Heat Resistant Materials for Hypersonic Leading Edge Applications".
2. Campbell, I. E., "Symposium on High Temperature, A Tool for the Future", Stanford Research Institute, Menlo Park, California (1956).
3. Hartwig, J., Pending U. S. Patent Application, Serial No. 843363.
4. Currie, L. M., Hamister, V. C. and MacPherson, H. G., Proc. Int. Conf. on the Peaceful Uses of Atomic Energy, Volume VIII, Paper PT 534, Geneva (1955).
5. National Carbon Research Laboratory Report, 3rd Quarter, 1962.
6. Waters, C. W. and Piper, E. L., WADD Technical Report 61-72, Volume XII, "Development of an Improved Large Diameter Fine-Grain Graphite for Aerospace Applications".
7. Balaguer, R. R., U. S. Patent 3,001,237.
8. GCR Quarterly Prog. Report, June 30, 1961, ORNL-3166, p. 96.
9. Bushong, R. M. and Kellar, A., U. S. Patent No. 2,761,848.
10. Private Communication from C. D. Pears, Head of Analysis and Measurements Section, Southern Research Institute.
11. Vought Astronautics Division, Ling-Temco-Vought Corporation, unpublished data.

9. APPENDIX: TEST METHODS FOR THE DETERMINATION OF PHYSICAL PROPERTIES OF GRAPHITE

1. Bulk Density. Bulk density was determined by dividing the mass of a specimen by its bulk volume. For graphite, the conventional unit is g/cc.
2. Specific Resistance. Electrical resistance was determined by measuring the potential drop along the length of a specimen with a given current flow.
3. Flexural Strength. Determined per ASTM Book of Standards, Test C-78-49, 3, 1323-1325 (1955). Sample size employed for tests discussed in this report was 1 x 1-1/2 x 8-inch, and was loaded at a rate of 250 lbs per minute. Flexural strength is calculated by means of the following equation:

$$S = \frac{3W(l_1 - l_2)}{2bd^2}$$

where W = load, lbs
 l_1 = length of lower span, inches
 l_2 = length of upper span, inches
 d = thickness of specimen, inches
 b = width of specimen, inches

4. Young's Modulus. The determinations were made by a sonic method, measuring the resonant frequency of vibration of the specimen supported at two points as a beam. A specimen of approximately 8-inch length and 1-inch thickness was employed. Young's modulus was calculated from the following equation:

$$E = \frac{178.6 K_s' f^2 W}{b}$$

where E = Young's Modulus, lbs/in²
 K_s' = a constant depending upon the thickness-to-length ratio of the specimen
 f = frequency, cycles/second
 W = weight of specimen, lb
 b = width of specimen, inch

5. Compressive Strength. Determined per ASTM Book of Standards, Test C-109-54T, 3, 129 (1955). The specimen was a 2-inch cube with flat end parallel faces.
6. Tensile Strength. Determined on a specimen 1/4-inch diameter x 1-1/2-inch gage length at a crosshead rate of 0.020 inch/min.

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7. Admittance. Determined by measuring the flow of a given gas through a specimen due to a pressure differential. Admittance was calculated from the relation

$$F = \frac{Q_{pv} l}{A \Delta_p}$$

where F = admittance, cm²/sec
Q_{pv} = pressure-volume flow, cc-atm/sec
l = length of specimen, cm
A = area of specimen, cm²
Δ_p = pressure differential across specimen, atm.

8. Thermal Conductivity. The longitudinal heat flow method was used where heat is introduced at one end of a specimen and flows through the specimen. The heat flow through the sample was measured by a differential thermocouple which gave directly the temperature differential between two points in the specimen. All measurements were made in vacuum on a specimen of 1/2-inch diameter x 5-inch length.
9. Thermal Expansion. The thermal expansion was determined over two temperature ranges: room temperature to 100°C, and 400 to 1000°C. The low temperature values were determined by clamping a 5-inch length of sample to one end of a similar length of reference material, and measuring the differential motion of the other end by an optical lever utilizing the rotation of a mirror mounted on a cylindrical rod separating the two materials. The high temperature values were determined by placing the specimen in a high temperature tube furnace and measuring the expansion of the sample by means of a traveling microscope. The change in length per unit length ($\Delta l/l$) was plotted vs. temperature.
10. Ash. The specimen was crushed to a powder, and a ten-gram sample taken. This sample was oxidized in air at 800°C until constant weight was obtained.

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